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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Results of sweeping experiments on synthetic quartz are presented. Sweeping was performed with an inert gas atmosphere below the transition temperature. An electric field of 1000 V/cm was employed. Alkali ions were observed to deposit on both electrodes. Doping was performed by sweeping alkali ions into the quartz. A Q-measuring technique was developed to evaluate the effects of sweeping and doping.

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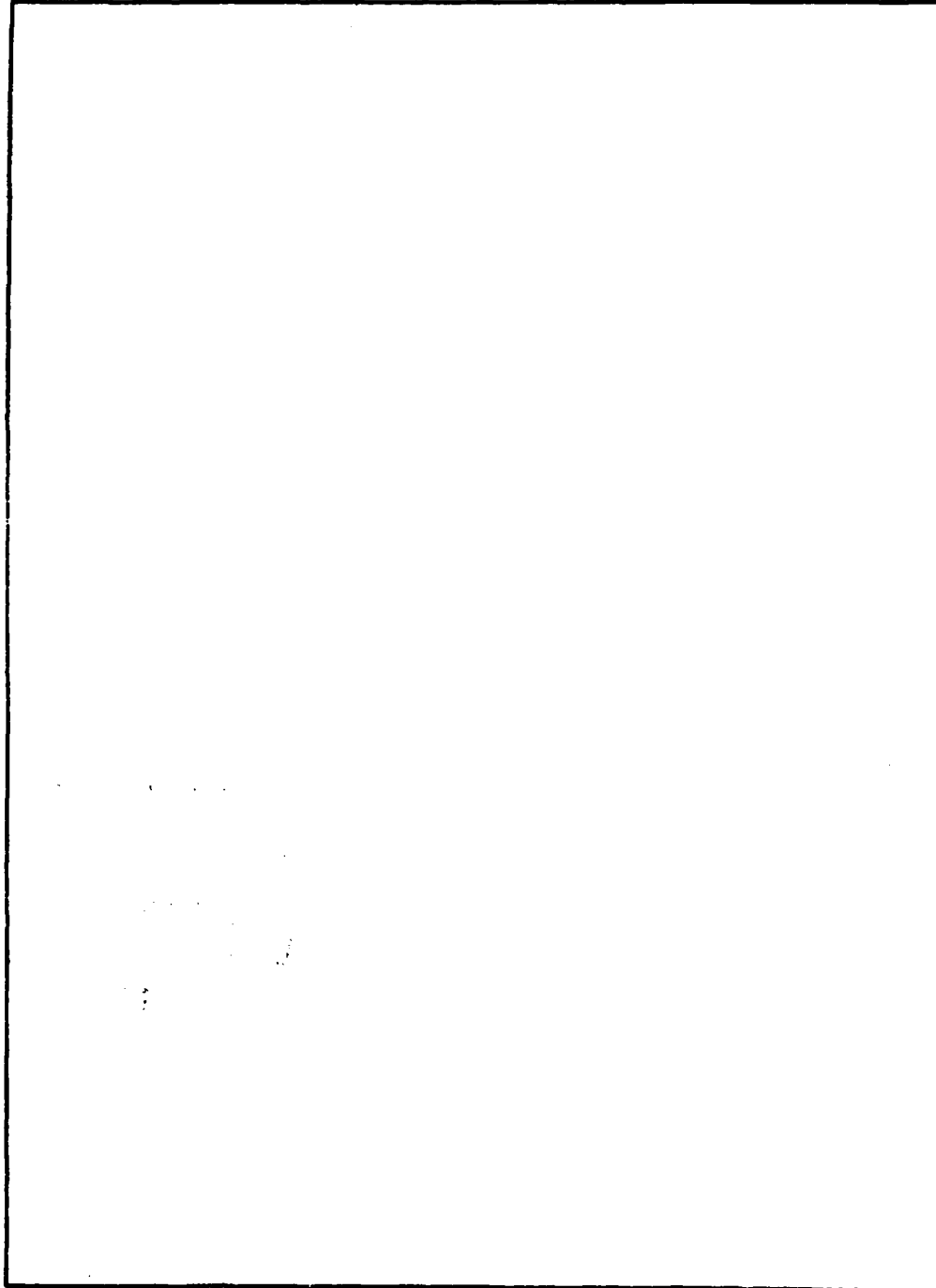, JAN 73

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Sweeping and Q Measurements at Elevated Temperatures in Quartz

1. INTRODUCTION

Quartz, natural and synthetic, is used in a wide variety of applications both
in the civilian and military markets. The principal civilian markets are CB radios,
watches and television. Military applications include communication and naviga-
tion systems, radio monitoring, and time code generators.

Natural quartz is available in various grades, but selection is generally based
only on visual observation of the raw material, with the result that the final device
may be unreliable due to flaws in the quartz. Synthetic quartz, on the other hand,
can be grown under reproducible and well-established conditions; devices grown
from synthetic material have a higher reliability. This reliability is sufficiently
high for most military and commercial uses. For some applications where a
higher quality device is needed, however, additional treatment following the
crystal growth process is required. The principal treatment presently employed
is called "sweeping" or solid-state electrolysis of the quartz prior to resonator
fabrication.

In the process of sweeping, quartz is brought to an elevated temperature; an
electric field is applied to sweep interstitial ions, principally sodium and lithium,
through the open channels along the Z-axis of the quartz structure. The ions are

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then deposited on the electrodes used to produce the field. The process has been shown to improve long-term stability, reduce radiation effects, and increase resonator Q values. [1]

This report contains the results of some electrolysis studies on quartz carried out at Rome Air Development Center, Solid State Sciences Division (RADC/ES). It includes descriptions of the sweeping apparatus, and an apparatus for measuring the Q of the swept samples, as well as the results of a series of experiments that shed some light on the effects of sweeping and doping on the Q of the quartz. First, however, we review some previous investigations of the process, its evaluation, and some of the effects produced by it.

2. PREVIOUS STUDIES

The majority of the significant studies on sweeping were performed early in the 1960's by J. King and D. Fraser at the Bell Telephone Laboratories. Their results have been summarized in a paper by Fraser. [1] These are the workers who correlated sweeping results with device properties. Doping, or the electrolysis of impurities into quartz, was performed as early as 1937 in work by Harris and Waring[2] who found ionic diffusion of lithium in fields as low as 55 V/cm at temperatures of $50°$ to $60°C$. These authors used their results to calculate the thermodynamic values of the diffusion process. They also quote an earlier reference (1888), indicating that sodium and lithium can be transported through quartz but that potassium cannot. Further, they found electrolysis limited to the principal Z-axis and attributed the lack of diffusion of the potassium ion to the large size of this ion as compared to the diameter of the crystallographic void parallel to the Z-axis. In 1950, Vogel and Gibson[3] investigated the migration of sodium ions through quartz under an applied field. These authors worked at a higher temperature, $210°C$, and used potentials up to 140 volts. About ten hours were required to reach a constant condition, indicating that sodium was migrating all the way through the crystal. They also confirmed that migration occurs only along the Z-axis of quartz. The plate thickness in these experiments was about 0.12 in. with the result that the applied field was about 460 V/cm.

The investigation of ions other than lithium, sodium and potassium has also been reported. Vanfleet et al[4] reported on the migration of silver ion under a

1. Fraser, D.B. (1968) Physical Acoustics, vol. V, Academic Press, N.Y., p. 59.

2. Harris, P.M., and Waring, C.E. (1937) J. Phys. Chem. 41:1077.

3. Vogel, R.C., and Gibson, G. (1950) J. Chem. Phys. 18:490.

4. Vanfleet, M.B., Baker, G.S., and Gibbs, P. (1963) J. Appl. Phys. 34:891.

field of 2000 V/cm at 400° to 560°C. The result of their experiments was decoration of the quartz by silver metal which, in some cases, caused the quartz to fracture. The decoration patterns for natural and synthetic quartz were different. These authors also reviewed the work of previous experimenters, reporting that calcium, iron, and aluminum salts would not transport, and that gold, platinum, aluminum, and copper metal likewise would not transport. Tin, lead, and bismuth were also tried unsuccessfully. Copper migration is of interest, since neither the metal nor the bipositive ion will migrate. However, the singly charged cuprous ion will migrate even though it is larger than the cupric ion. Thus, the charge on the ion seems to be more important than the ionic size.

The role of hydrogen or hydroxide in the sweeping process has been discussed by Brunner et al.[5] It is postulated that in order for sweeping to occur easily, hydrogen in the form of water vapor must be present. Hydrogen replaces the ions removed by sweeping; these ions are assumed to be loosely bound to a Group III impurity (usually aluminum), replacing silicon in the lattice. Since the proton is not stable in the interstitial position, it combines with one or two nearby oxygens in the lattice to form a hydroxide or hydrogen bond. However, the actual mechanism involved in withdrawing the hydrogen ion from water is not clear, but it may be related to some type of surface catalysis. It has been reported by some authors[1] that it is more difficult to sweep quartz under high vacuum. The formation of color centers in vacuum sweeping has also been reported. This is considered to be the effect of a combined vacancy-aluminum ion combination resulting in a "A" type color center.

The effectiveness of the sweeping process has been analyzed in two principal ways: low temperature infrared absorption spectra and resonator Q measurements. Using resonator Q measurements, King[6] established that the sweeping process produced an order of magnitude improvement in quartz at all temperatures except in the region from 210° to 250°K where the swept material had a slightly lower Q. Several loss peaks were produced along the profile which King attributed to impurities and dislocations. Using doped samples, Dodd and Fraser[7] measured the infrared absorption at 77°K and in consequence, they were able to assign certain impurities, as well as Si-0 vibrations, to the various loss peaks. They also performed experiments showing the absorption decreases when a sample is swept in air rather than vacuum. As previously stated, one must keep in mind that

5. Brunner, G.O., Wondratschek, H., and Laves, F. (1961) Z. Elektrochem. 65:735.

6. King, J.C. (1959) Proceedings of the 13th Annual Frequency Control Symposium, Electronic Industries Assoc., Washington, D.C., p. 1.

7. Dodd, D.M., and Fraser, D.B. (1965) J. Chem. Phys. Solids 26:673.

absorptions are due to hydroxide radicals bonded differently to the various impurities as well as to the silicon. In most of the infrared and resonator Q measurements, the amount of impurity has been estimated from analysis. However, the results do not correlate with the other measurements, since many of the impurities go into inactive sites and into inclusions within the quartz. These inactive impurities may account for 95 percent of the total impurity concentration.[8]

The mechanical Q is evaluated commercially by determining the room temperature infrared absorption at a wave number of 3500 cm^{-1}. This is based on work by Rudd et al in 1966.[9] These authors generated a curve of the extinction coefficient versus the mechanical Q which is used as the standard. These curves have a limited reliability above a Q of one million, however. The work of Rudd et al was based entirely on hydroxide grown quartz. The curve generated from carbonate solutions is somewhat different. It should be mentioned also that the optical Q evaluation is valid only for unswept crystals. On sweeping, more hydroxide is introduced, replacing alkali metal ions during the process. The net result is a higher absorption but a higher Q.

In recent years, Japanese workers[10,11] have been studying the relationship between Q measured in resonators with the infrared Q and with dislocations and inclusions. Their research indicates that if Q has a value greater than 1.9×10^6, inclusions and dislocations are insignificant. They were unable to get a definite relationship between the dislocations or changes of d-spacing (measured with doubly diffracted X rays) with Q. They use the 3580 cm^{-1} peak for their infrared Q, rather than the 3500 cm^{-1} used in the United States. However, it was indicated in their work that the infrared Q at high values is not necessarily reliable, since there is not always an increase in the Q of the finished crystal unit. This may also be associated with losses in the unit fabrication.

3. SWEEPING PHENOMENA

There are four stages occurring during sweeping,[12] described as follows:

1. Displacement current, decaying between 10^{-1}-10^{-2} sec, (due to normal dielectric charging).

8. Rybach, L., and Laves, F. (1967) Geochimica et Cosmochimica Acta 31:539.

9. Rudd, D.W., Houghton, E.E., and Carroll, W.J. (1966) The Engineer, Western Electric, 22.

10. Asahara, J., and Taki, S. (1972) Proceedings of the 26th Annual Frequency Control Symposium, Electronic Industries Assoc., Washington, D.C., p. 93.

11. Asahara, J., et al (1974) Proceedings of the 28th Annual Frequency Control Symposium, Electronic Industries Assoc., Washington, D.C., p. 117.

12. Wenden, H.F. (1957) Am. Mineral. 42:859.

2. Anomalous charging current (which appears on changing the potential and lasts about 15 minutes).

3. Surge current (attributed to impurity ion migration and lasting several hundred hours).

4. Steady-state current (attributed to electrolytic dissociation of quartz).

In general, evidence of these stages is present in all sweeping runs. The part of most interest in sweeping, obviously, is the surge current due to impurity migration. The rate-determining step for the surge current does not appear to be migration of the impurity ion through the quartz, but transport from the surface of the quartz to the electrode. This has been substantiated by several workers who find comparatively large amounts of impurity ions, principally lithium and sodium, on the cathode surface of the quartz. Similar results were found in this study.

For the past ten years, since commercial production became routine, little research on sweeping or Q evaluation has been reported. Problems related to resonator performance resulted in some additional sweeping and considerable Q evaluation about five years ago, [13] and these studies have led to the present program at RADC/ES. Some sweeping studies conducted under an Air Force grant[14] indicated that potassium could be swept into the lattice at $500^{\circ}C$, but the final concentration of the impurity ion was not evenly distributed.

4. DESCRIPTION OF THE RADC/ES SWEEPING APPARATUS

Previously developed sweeping processes have used either air or vacuum as an ambient. At RADC, it was decided that the most reproducible ambient was inert gas, dried before passing into the sweeping system. A schematic diagram of the apparatus is shown in Figure 1 and a photograph in Figure 2. The furnace is made with an alundum core using Kanthal wire wound around the outside. A Chromel-Alumel thermocouple is placed at the midpoint and the assembly is enclosed by several layers of Fiberfrax blanket. A 50-mm diam. quartz tube is inserted into the furnace with the ends extending about 12 in. beyond the end of the furnace. The ends of the tube are closed with neoprene stoppers through which small tubes have been inserted to conduct the flushing gas, support the sample holder, and lead out the wires from the electrodes. The sample holder (shown in the insert in Figure1) is made of boron nitride with coiled Elginol springs to assure good pressure contact between the electrodes and the sample. Elginol is used

13. Brown, R. N., and Kahan, A. (1975) J. Phys. Chem. Solids 36:467.

14. Halperin, A., Levinson, J., Braner, A., et al (1973) Final Scientific Report, Hebrew University, Jerusalem, Grant AFOSR 72-2366.
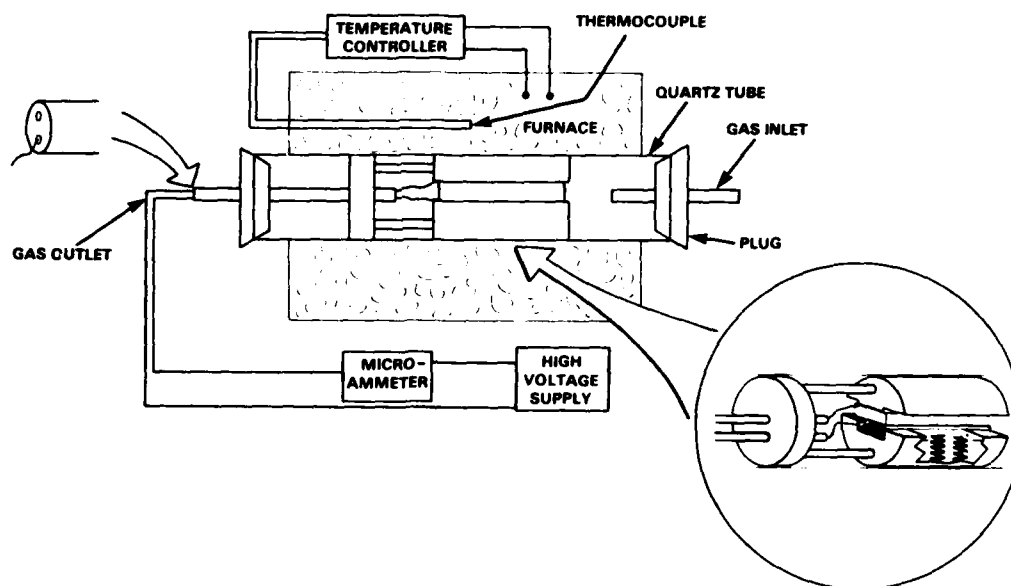
Figure 1. Schematic Diagram of Sweeping Apparatus
(insert shows holder assembly)

because it retains its elasticity at higher temperatures and is not easily oxidized.
The electrodes are cut from platinum sheets and welded to the platinum wire that
passes through the end stoppers.

The output of the furnace thermocouple is compared with a set point voltage,
and power is applied to the furnace windings in response to voltage variations. In
this way, the temperature of the furnace can either be held constant or be in-
creased or decreased by programming the bucking voltage. An L&N Trendtrak
system is used for this purpose.

Two ambient gases, nitrogen and argon, are employed. In performance of
the usual sweeping experiments, nitrogen gas from a liquefied nitrogen source
was used. Nitrogen was found to be less susceptible to arcing than other gases.
In cases where doping by electrolysis is performed, argon gas passed through a
titanium getter at $800^{\circ}C$, is used in place of nitrogen. The substitution of argon
serves to eliminate the remote possibility of nitride formation.

A high voltage DC power source is used to apply the electric field between the
electrodes, placed on the opposite Z faces of the sample. A small resistor is
placed in series with the sample and the voltage on the resistor is recorded to
monitor current passing through the quartz. It is assumed that all current passes
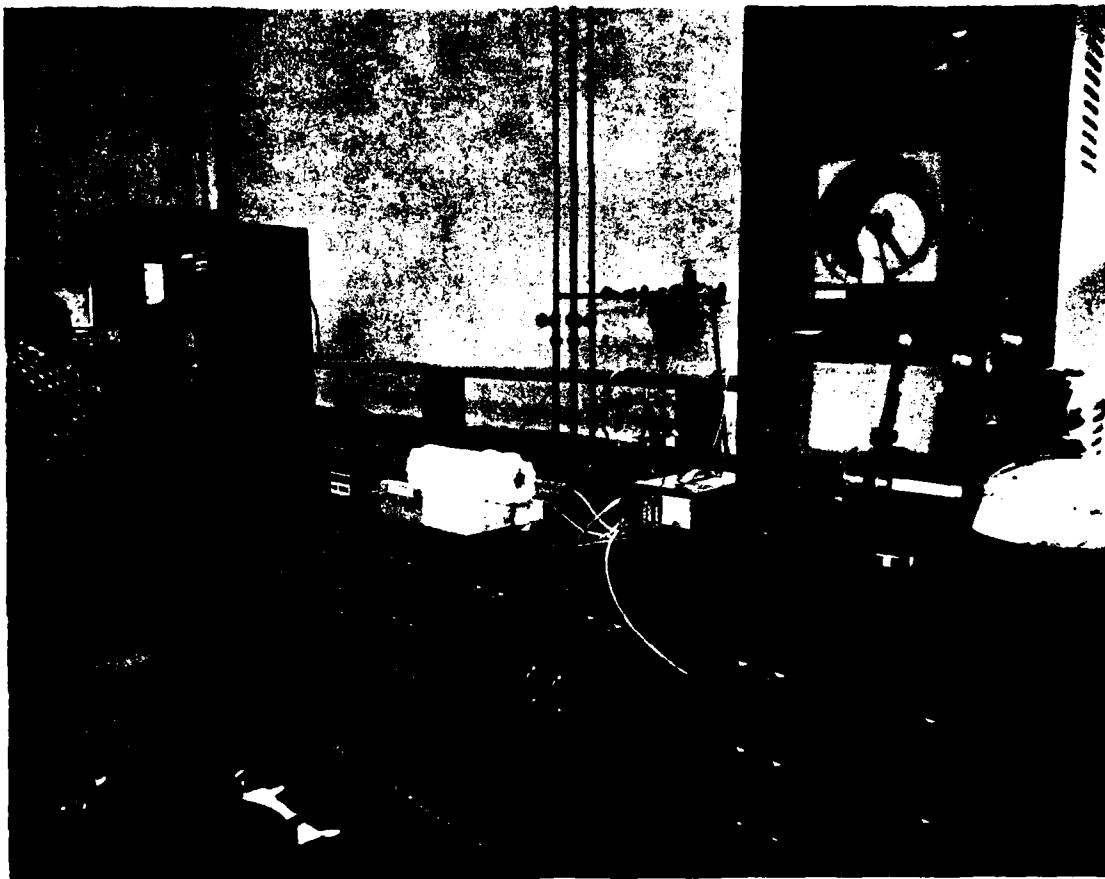through the quartz with no surface current being produced.

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Figure 2.   Photograph of RADC/ES Sweeping Apparatus

5. SWEEPING PROCEDURES

For fabrication into resonators, samples are cut from single crystal boules:
the samples have the following approximate dimensions:

$X = 2$ cm, $Y = 5$ cm, and $Z = $ at least 1.5 cm .

An attempt is made to have only Z-growth material in the sample, but subsequent
analysis of some bars indicates that some X-growth material is also present. The
four larger faces are ground and polished to assure good contact with the electrodes
and allow visual and infrared inspection. The electrodes are placed so as to apply
the electric field along the Z-axis.

In addition, some AT-cut samples were used to facilitate the Q measurements.
These were in the form of plates of approximate size $2.0 \times 1.7 \times 0.2$ cm, the large
faces being the AT cut. The electrodes were parallel to the large faces, so that
the field made an angle of $\sim 55^{\circ}$ with the Z-axis.

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In most cases, samples are treated with the application of a thin sputtered layer of platinum on the Z faces to improve the electrical contact with the electrodes. There are some indications that this improves the sweeping efficiency. After the sample is prepared and placed in the furnace, the temperature is gradually raised to 550°C over a period of 24 hours. Heating is done slowly to prevent cracking of the quartz. The same procedure is used to cool the quartz to room temperature after sweeping. The field is left "on" during cooling. Later experiments were performed at 500°C and the warm-up time was changed to 48 hours, when it was learned that some swept bars shattered during resonator fabrication. It was surmised that the higher temperature may fall within the range of uncertainty of the transition temperature where the quartz changes from the α to the β form. The transition temperature for pure quartz has been established as 573°C, but the transition has been observed to occur as low as 535°C in some impure specimens.[15] In the return from β to α quartz upon cooling, cracks can develop. These could later cause the observed shattering. Even if the transition temperature is not reached, too rapid heating or cooling could cause cracks; hence the warm-up time was doubled as an additional precaution.

With the sample at 500° or 550°C and while being flushed with inert gas at a rate of 0.1 liter/min, the voltage is gradually applied from zero and the current monitored in order to prevent excessive Joule heating of the quartz sample. With the size of the sample used, 100 mW is considered to be a safe level. The voltage is raised to at least 1000 V/cm. The current decreases with time and the run is terminated when the rate of decrease has leveled off to zero. At this point, the sample is cooled, about 30 microns of each Z face is ground off and polished; the sample is replaced and the process repeated. An outline of this procedure is shown in Table 1.

Table 1. Sweeping Procedure

• Evaporated platinum electrodes
• Nitrogen ambient (0.1 liter/min)
• Heat up - (48 hours)
• Sweep at 500° to constant current
• Cool down - (48 hours)
• Grind 30 microns off surfaces and repeat

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15. Frondel, C. (1962) The System of Mineralogy, vol. III, Wiley, N.Y., p. 118.
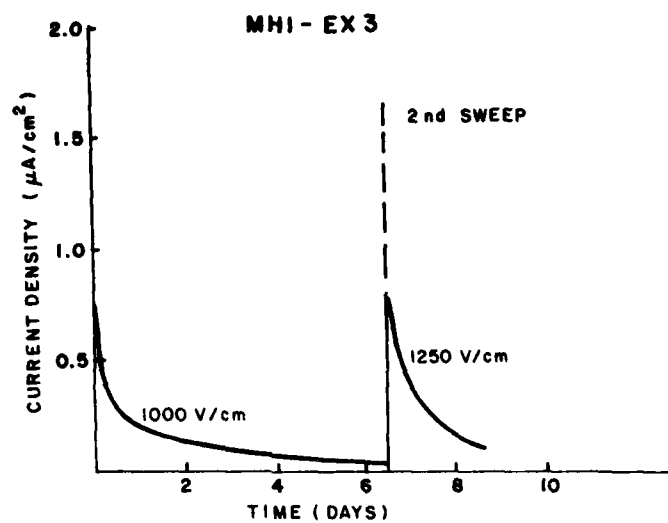
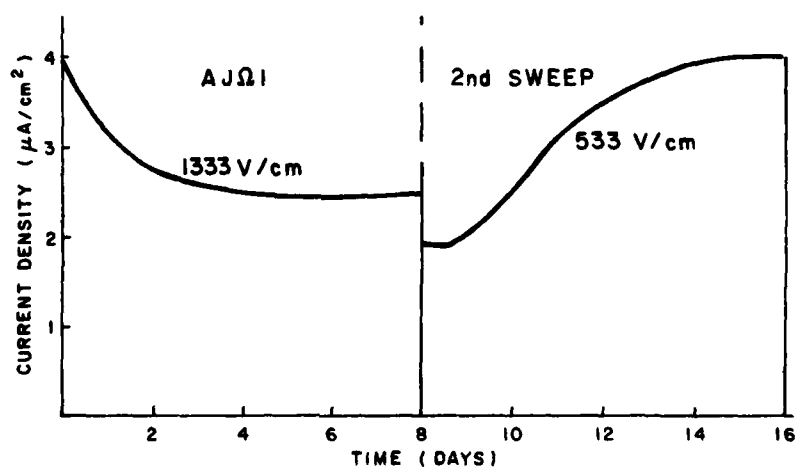Figure 3. Typical Variation of Current Density with Time of Sweeping

Figure 4. Abnormal Variation of Current Density with Time of Sweeping

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After each run, the electrodes were held in a flame, and each showed the presence of sodium by its characteristic color, with a preponderence on the cathode.

A curve of current versus time for a normal sweeping run is shown in Figure 3. In some cases, the second sweep does not behave in the normal fashion, but undergoes a current increase with time (Figure 4). The cause of this is not known, but similar results have been reported by other workers.[16] Figures 3 and 4 are regarded as relative rather than absolute curves, particularly at the zero time end, because the rapid initial surge is too large for accurate measurement on this equipment. An added uncertainty is due to surface effects which have been assumed to be negligible.

6. DOPING

Doping of a sample is done in essentially the same manner as sweeping. Argon gas is used in place of nitrogen as discussed earlier. Samples to be doped are first swept using the standard procedure, except that the samples are swept only once. After sweeping, a salt of the material to be used is coated onto both surfaces under the platinum electrodes, and the sample is heated to $500^{\circ}C$.* The field is then applied and electrolysis commences. In this case, the current increases with time. The run is terminated after a charge density of about 2 coulombs/cm^3 has been transported. The sample is then annealed at $500^{\circ}C$ for roughly six weeks, in order to achieve a more uniform distribution of alkali ions, since the ion density after electrolysis is expected to be much higher at the surface than at the center of the bar.

Electrolysis has been performed using lithium, sodium, and potassium salts. Representative results appear in Figures 5 to 7. All the curves show larger current with the salt applied to the surfaces; the smaller the atomic weight of the alkali ion (and the ionic radius), the larger the current. Order of magnitude estimates of conductivity can be read from these curves, yielding 10^{-6} (ohm-cm)$^{-1}$ for lithium, 10^{-8} for sodium and 10^{-9} for potassium. These experiments were performed at $550^{\circ}C$.

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16. Young, T.J. (1978) Private communication.

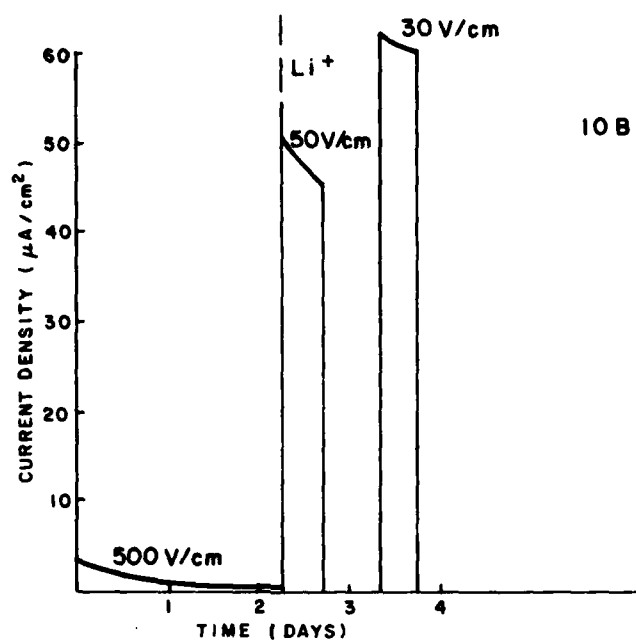*In some of the early runs $550^{\circ}C$ was used.
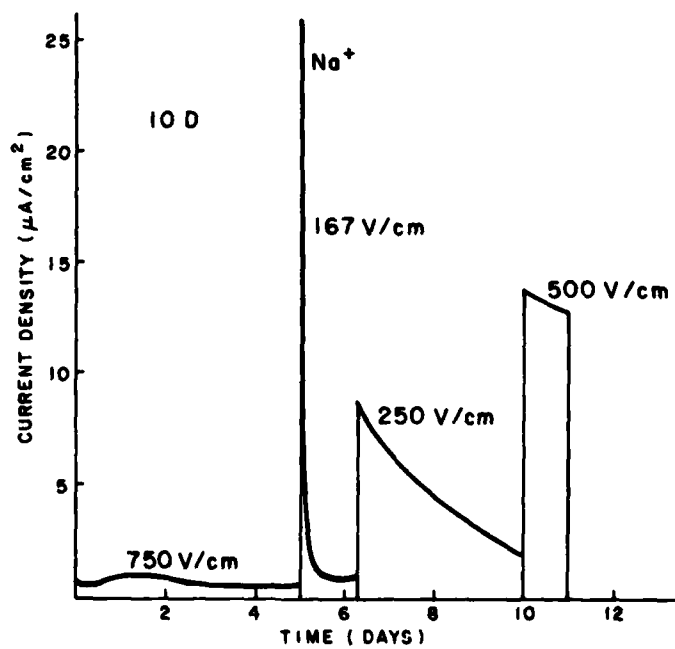
Figure 5. Current Density Curve for Lithium

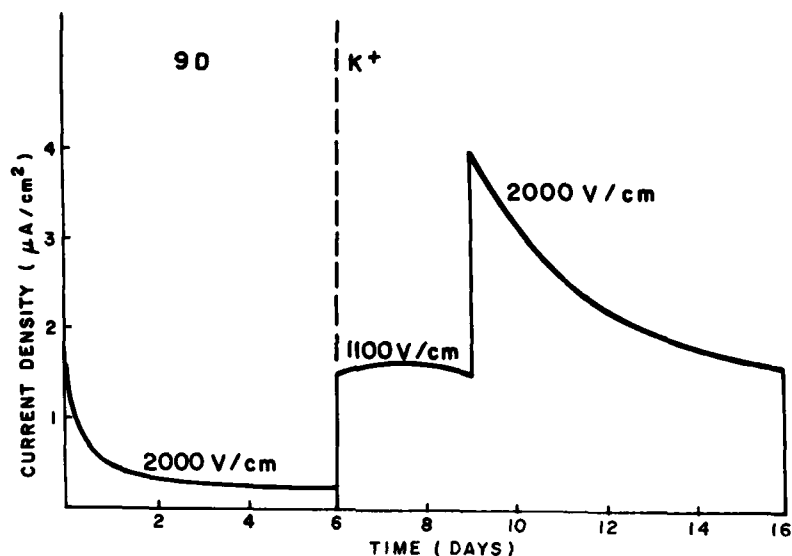Figure 6. Current Density Curve for Sodium

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Figure 7. Current Density Curve for Potassium

7. Q MEASUREMENT APPARATUS

An apparatus for the measurement of Q was assembled for the purpose of rapid evaluation of the sweeping and doping processes. The optimum technique for Q measurement is the fabrication and testing of a finished resonator, either sealed in glass or measured by the ceramic gap holder technique.[1] Since fabrication is necessary, this is a time-consuming process (often months), which is also expensive. The technique used in this report was more rapid, but less quantitative. Initially, the large bars being swept for production of resonators were measured, using the fundamental lengthwise compressional mode excited by electrodes on the X faces, but mounting difficulties precluded the possibility of obtaining reproducible results. The bars were held with knife edges midway along the length, where a vibration node existed.[17] The knife edges served also as electrical leads, and the surfaces in contact with the knife edges were plated with platinum. The nodal line was found by trial and error, noting the output voltage and frequency each time the position was changed, until a maximum voltage and minimum frequency were obtained. It proved to be impossible to achieve repeatedly the same maximum amplitude by this method; thus a different configuration was sought, since the purpose was to compare results before and after sweeping. A configuration

17. Cady, W. G. (1964) Piezoelectricity, Dover Publications, Inc., N.Y., p. 95.

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consisting of a thin plate resting on one electrode with a gap above it had been tried successfully in the past, [1] and was therefore used, as it appeared to afford reproducibility. We rejected X- and Y-cut samples, because they cannot be swept, and a Z-cut cannot be excited piezoelectrically. An obvious choice, then, is the AT-cut, since the resonators are fabricated from this cut. The sample is positioned between platinum-coated surfaces of a lavite holder, these surfaces serving as electrodes, with an AT-face resting on one surface. There is a gap of about 1 mm width between the sample and the other electrode. The assembly is held between two windings of Kanthal wire in another lavite holder, used for heating the sample by radiation. The entire assembly resides in a Veeco evaporator, evacuated to a pressure of about 50 μm of Hg. A Pt-Pt (10% Rh) thermocouple is placed near the sample to monitor its temperature, and a Chromel-Alumel thermocouple is used for temperature control.

The sample is connected to a transmission circuit, a schematic of which is shown in Figure 8. The sample is excited at the resonant frequency with a synthesizer and the output voltage of the transmission network is measured with an AC voltmeter. The termination resistors R_t are each 47 ohms, and the isolation resistors R_i are each 470 ohms. [18] This circuit was chosen because of its
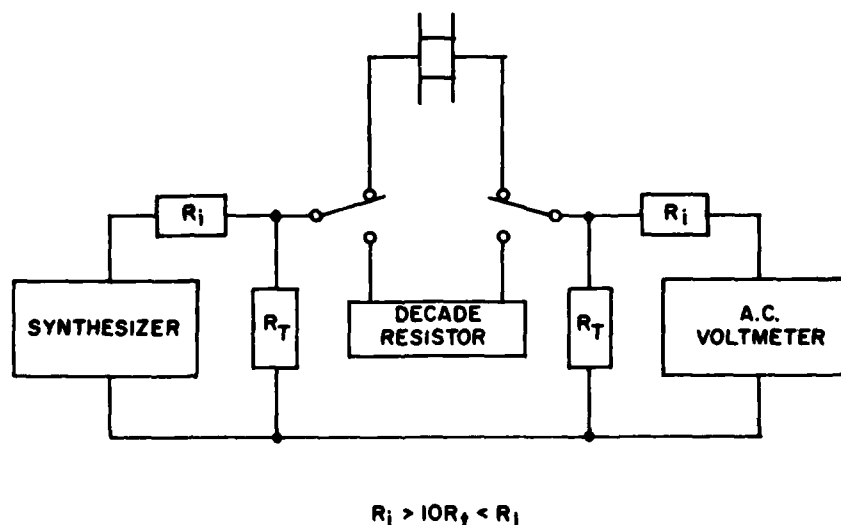

$$R_i > 10R_t < R_i$$

Figure 8. Block Diagram of Transmission Circuit Used in the Q Measurements

18. Gerber, E. A. and Koerner, L. F. (1958) Proc. IRE 46:1731.

simplicity and because it is the basis of an IEEE standard.[19] A photograph of the apparatus is shown in Figure 9.
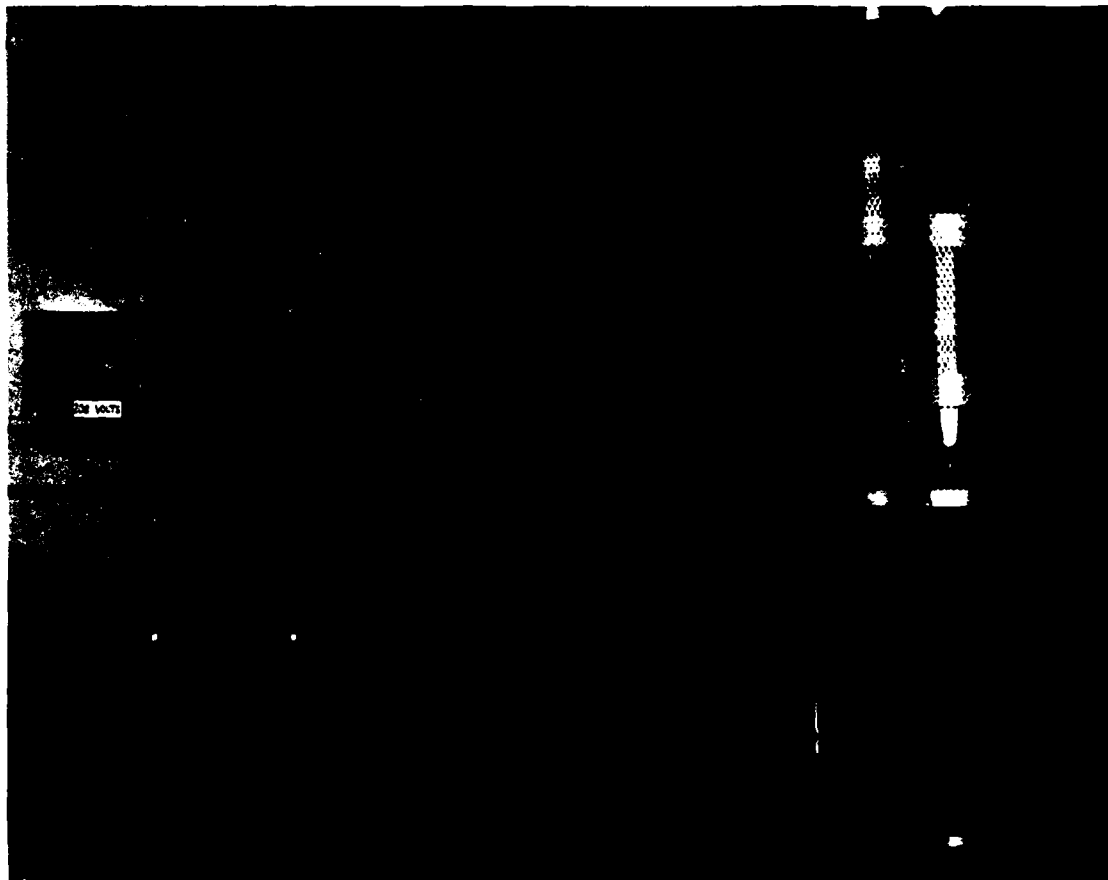

Figure 9.   Photograph of the Q Measuring Apparatus

B. METHOD OF MEASUREMENT

There are several methods of measuring the Q of the quartz plate with the circuit described. All of them involve varying .he frequency of the synthesizer until a maximum output voltage is found. This is the resonant frequency f_s corresponding to zero reactance in the resistive branch of the equivalent circuit.

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19. Standard Definitions and Methods of Measurement for Piezoelectric Vibrators (1966) IEEE No. 177.

18

The method chosen involves measuring the frequencies at the half-power points on either side of the resonance peak, and determining Q in terms of the difference of these frequencies Δf as follows:[20]

$$Q = \frac{f_s}{\Delta f} \left(1 + 2 \frac{R_t}{R_1} \right) \approx \frac{f_s}{\Delta f} \ .$$

The approximation is valid for the plates measured, since values of the resistance R_1 measured by substitution, are large compared to the termination resistance R_t.

There is a resonator current value that corresponds to a strain that is sufficient to break the crystal. A rule of thumb[21] limits the current density with thickness vibrations to 20 mA/cm^2, referring to electrode area. The minimum impedance of the circuit (at resonance), for all values of R_1, is roughly $R_i = 470$ ohms. With an input voltage of 2 V, the maximum total current in the circuit is about 4 mA, the resonator current being considerably less than this. With an electrode area of $2.0 \times 1.7 = 3.4$ cm^2, the resonator current density is less than 1 mA/cm^2, well below the limit.

As the synthesizer frequency is varied through resonance, the output voltage of the transmission circuit goes through a sharp peak, followed at a higher frequency by a dip as shown in Figure 10. The peak corresponds to series resonance, whereas the dip corresponds to a maximum in the equivalent series resistance.[19]

The resonant frequency multiplied by the plate thickness is known as the wave constant, expressed in kHz - mm. For the plates used in this work, all being approximately the same thickness, an average value for the wave constant is 1711 kHz - mm.

Observations of the output voltage at resonance both at atmospheric pressure and at a pressure of 50 μm show that there is a loss to the surrounding air, an acoustic wave being excited in the adjacent air by the vibrating plate. This is manifested by an increase in the output voltage as the air pressure is reduced. The output voltage increases by a factor between 2 and 3.

20. Gerber, E.A. (1953) Proc. IRE, p. 1103-1112.
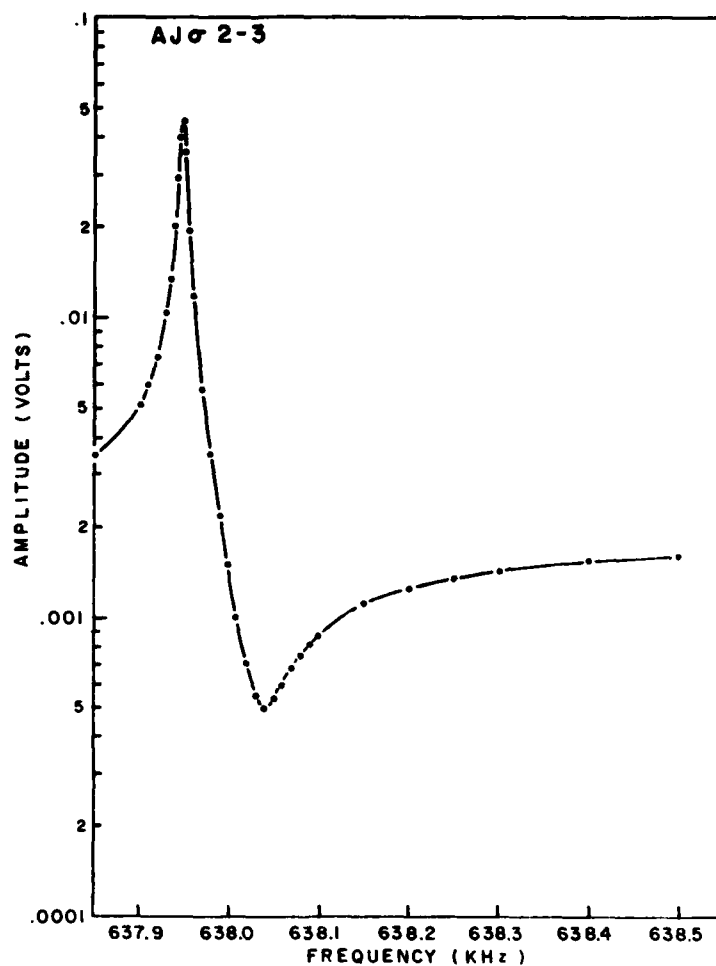21. Cady, W.G. (1964) Piezoelectricity, Dover Publications, Inc., N.Y., p. 325.

Figure 10. Typical Output Voltage Curve vs. Frequency

9. RESULTS

The Q measurements were made at a temperature interval of approximately 20° from room temperature up to $300^\circ C$. The output voltage of a Chromel-Alumel thermocouple in close proximity to the sample was monitored on a strip chart recorder, and a measurement of frequencies made when the temperature had stabilized. The reciprocal of Q, representing the loss due to internal friction in the quartz plate, is then plotted as a function of temperature. In this way, the curves of Figure 11 were generated. This shows the reciprocal Q of a sample before sweeping, after sweeping 1 day, and after sweeping 2 weeks. Not only

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is the broad loss peak around 205°C removed after 1 day, but the entire temperature range shows reduction of loss, and further reduction is achieved after 2 weeks of sweeping. This first sample, as were all the samples used for Q measurement, had been cut from a bar of premium Q quartz designated AJσ2.

A second sample shows two loss peaks: at 165° and 215°C before sweeping, and a flat curve after sweeping 2 weeks (Figure 12). This latter curve is very similar to the 2-week curve for the previous sample (Figure 11), including the rise at the high temperature end.

Figure 13 shows the results for a third sample, with loss peaks at 170° and 240°C before sweeping, and a curve very similar to the 2-week curves after sweeping only 4 days.

A fourth sample, Ajσ 2-1 (results not shown), exhibited a curve resembling the 2-week curves both before and after sweeping 3 days. This sample was subsequently doped with lithium by coating one surface with a water slurry of Li_2CO_3, and sweeping until a charge density of about 2 coulombs/cm^3 had been transported, as determined by the monitored current. The results are shown in Figure 14, where it is seen that a sharp rise at the high temperature end is introduced by the doping.

A fifth sample was similarly doped with sodium by using a slurry of NaCl; the results are shown in Figure 15. Here the loss is increased over the entire temperature range with a general rise with increasing temperature.

A sixth sample was doped with potassium, using a KCl slurry, resulting in the introduction of a loss peak at 242°C (Figure 16).

In order to check the reproducibility of the measurements, a series of sweeping and measurement was performed with lithium and sodium. In this series, samples were first swept, then doped with lithium and sodium. The samples were then swept again and redoped with the other cation as follows:

SAMPLE A: Swept, doped with lithium; swept, doped with sodium.

SAMPLE B: Swept, doped with sodium; swept, doped with lithium.
After each step, Q measurements were performed. The results are shown in Figures 17 and 18.

Both Figures 17 and 18 show a trend toward higher losses each time a crystal is processed, irrespective of which alkali ion is being diffused in. There is an indication that some loss peaks in the unswept sample, may have been restored by lithium doping, as seen by comparing Figures 12 and 18.

To elucidate the effect of temperature on the sweeping process, two samples were swept at 500°C and at 550°C, and Q measured after each sweep. The results are shown in Figures 19 and 20. It may be seen that sweeping at 500°C yields a higher Q. In order to eliminate the sequential factor, one of these samples was swept first at 550°C, then at 500°C, while the other was swept first at 500°C.
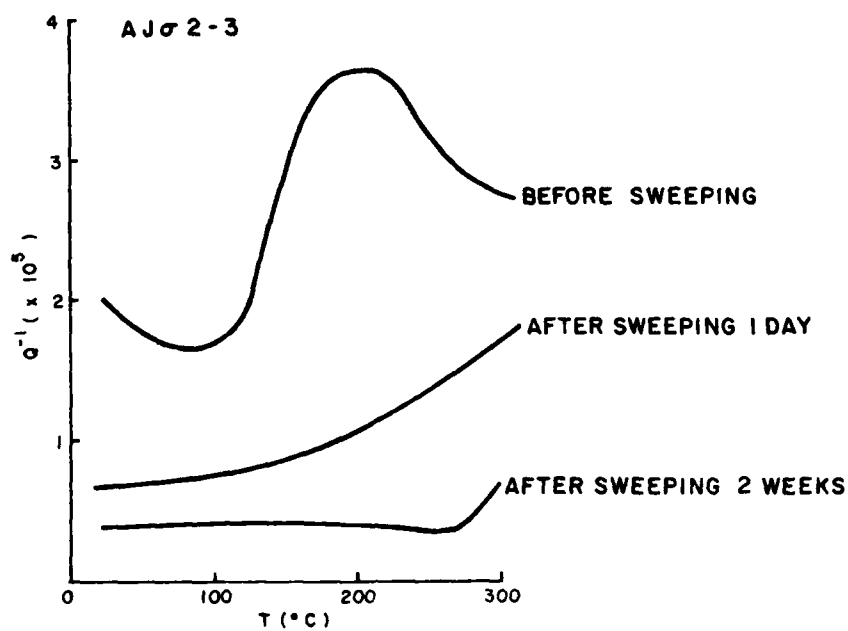
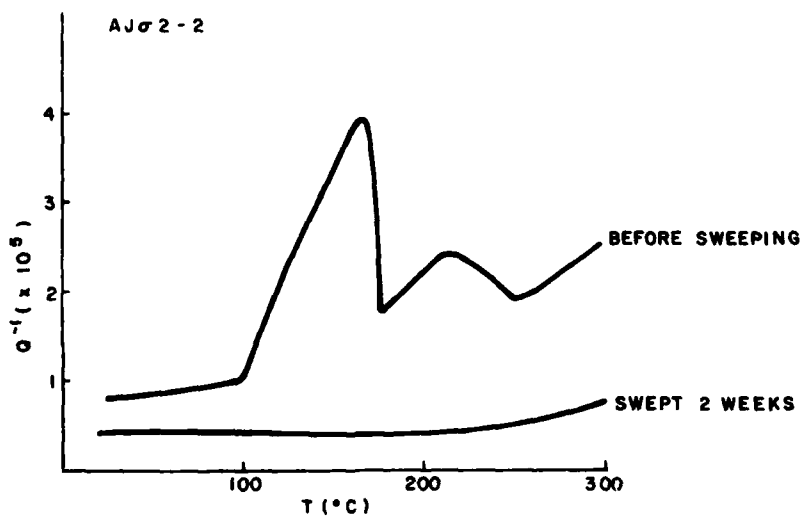Figure 11. Q^{-1} vs. Temperature, Showing the Effect of Duration of the Sweep

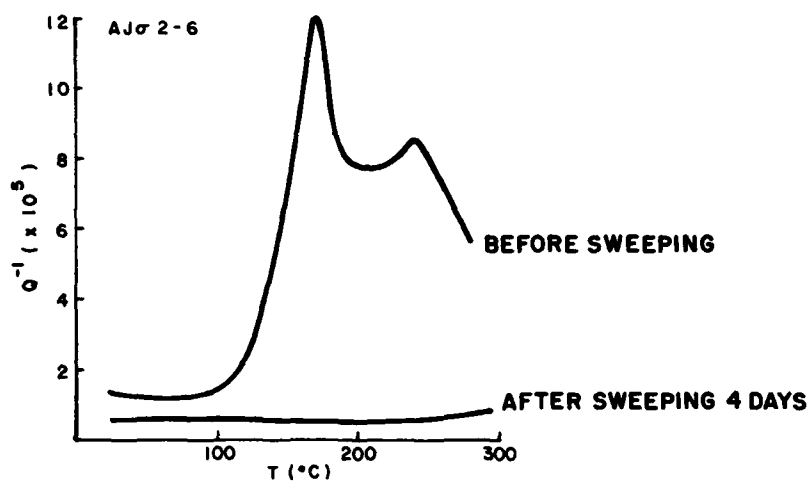Figure 12. Q^{-1} vs. Temperature Before and After Sweeping

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Figure 13. Q^{-1} vs. Temperature, Showing the Effect of
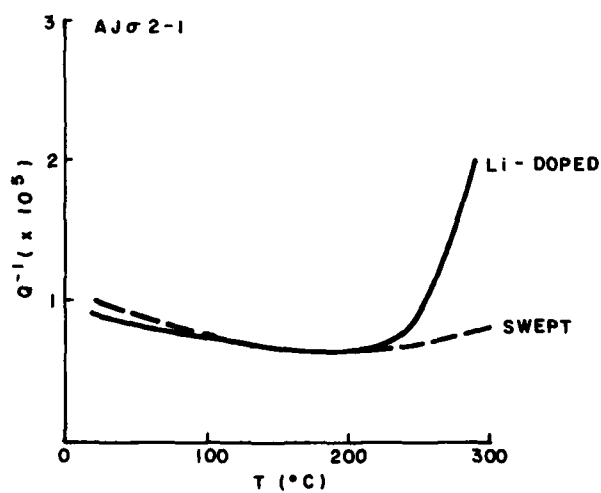Sweeping Only Four Days

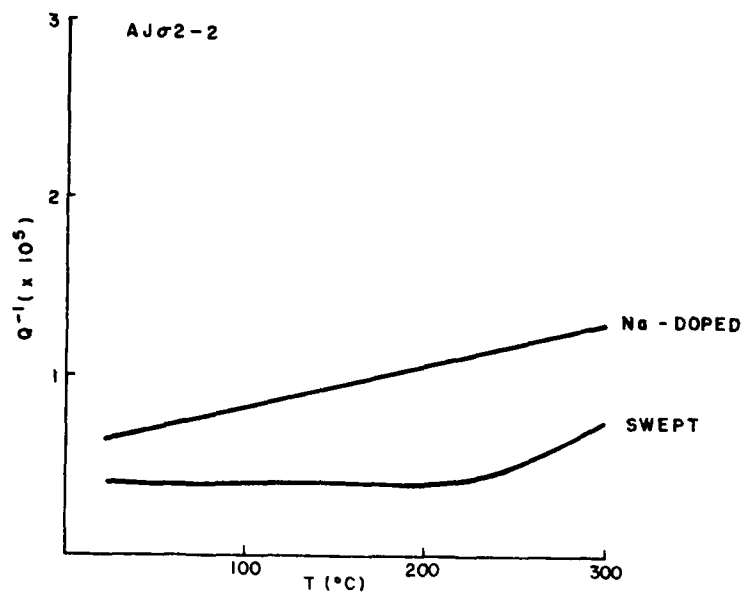Figure 14. Q^{-1} vs. Temperature, Showing the Effect of
Doping with Lithium

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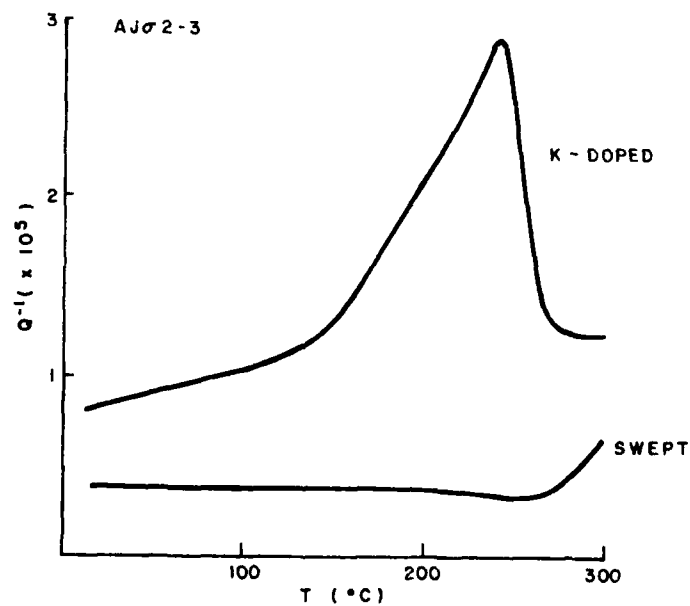Figure 15. Q^{-1} vs. Temperature, Showing the Effect of Doping with Sodium

Figure 16. Q^{-1} vs. Temperature, Showing the Effect of Doping with Potassium
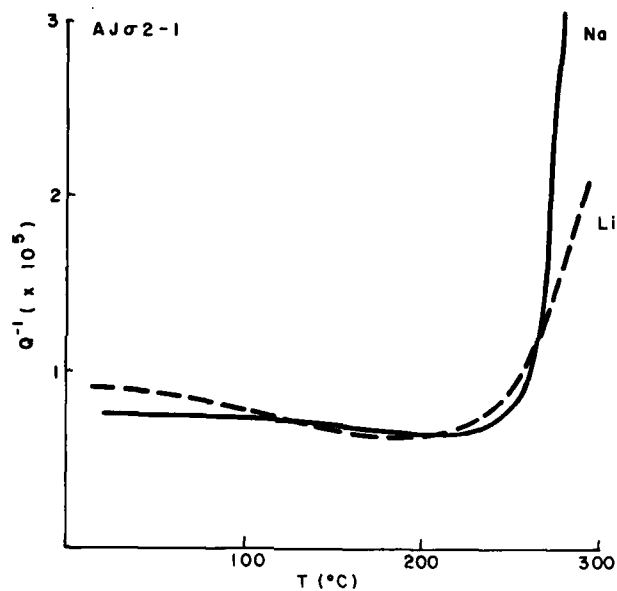
24

Figure 17. Q^{-1} vs. Temperature, Showing the Effect, in One Sample. First doping with lithium; then with sodium
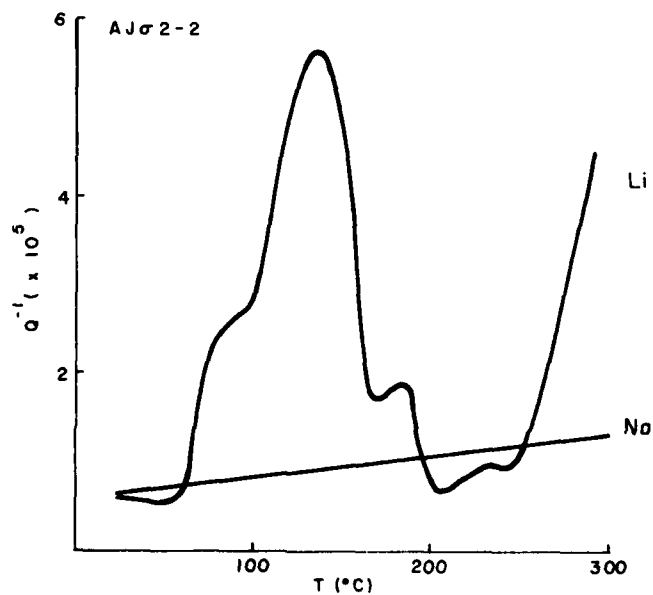

Figure 18. Q^{-1} vs. Temperature, Showing the Effect in One Sample. First, doping with sodium; then with lithium
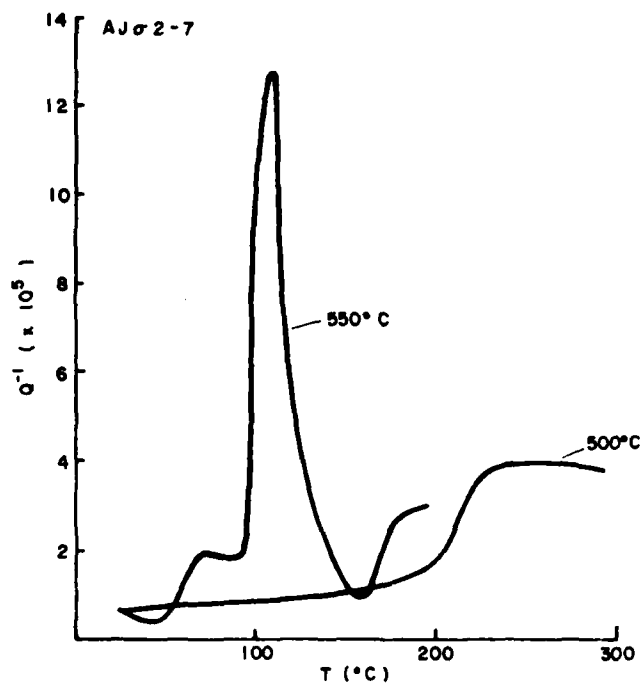
25

Figure 19. Q^{-1} vs. Temperature, Showing the Effect of Sweeping in One Sample. First at 550°C; then at 500°C
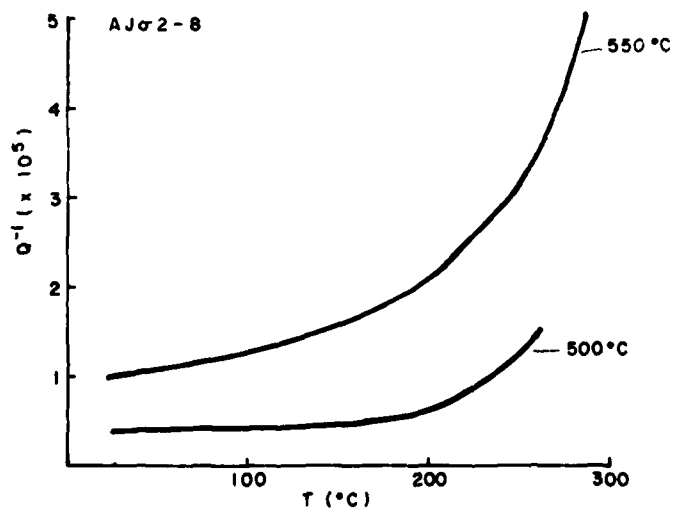

Figure 20. Q^{-1} vs. Temperature, Showing the Effect of Sweeping in One Sample. First at 500°C; then at 550°C

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10. DISCUSSION

It is believed that the Q^{-1} value deduced from these measurements contains contributions from sources other than the quartz, for two reasons: First, it is expected that a loss will appear, due to the contact between one surface of the quartz plate and the electrode on which it is resting, although the magnitude of this loss is unknown; second, calculations of Q based on measurements of the resistance R_1 and motional capacitance C_1 have not yielded consistent values. It is suspected that improvements in the circuit stray capacitance could be achieved.

Nevertheless, some observations can be made about the Q measurements. First, the effects of sweeping on previously unswept material can be observed. For example, an improvement of Q in relation to sweeping duration is apparent in Figure 11, where the results after 1 day and 2 weeks are shown. Generally, it is observed that sweeping, independently of the duration, yields some improvement in Q. Doping, on the other hand, as indicated in Figures 14 to 16, appears to introduce additional losses, even in the case of potassium.

The results of the double doping with sweeping between the doping runs are not clear (Figures 17 and 18). We observe that the curves produced by alternate doping appear to be more characteristic of the sample than of the cation; that is, the loss rises sharply with increasing temperature in sample $AJ\sigma2-1$ (Figure 17), whether it is doped with lithium or sodium, whereas different behavior is observed in sample $AJ\sigma2-2$ (Figure 18). Here only a gradual rise with increasing temperature is seen when this sample is doped with sodium, and a complex pattern is observed with lithium doping.

These variations could be due to sweeping factors related to the quartz, such as impurities collecting in inclusions or other imperfections. However, it appears more likely that the measurement problems discussed earlier are responsible.

The single most consistent feature of the data is the general rise in Q^{-1} at the high end of the temperature range. This agrees with some earlier studies of Cook and Breckenridge,[22] who found a peak above $300^{\circ}C$ in bars vibrating in a lengthwise compressional mode.

11. CONCLUSION

The results reported here have shown that removal of a 30 μm layer of quartz at the surfaces of a swept bar increases the current during a subsequent sweep of the same bar. This tends to confirm the hypothesis that the mobile ions accumulate near the surface, and the rate-determining step in the process is the transport of

22. Cook, R. K., and Breckenridge, R. G. (1953) Phys. Rev. 92:1419.

the ions from the quartz surface to the electrode. Furthermore, the flame tests show that sodium ions are being deposited on the electrodes during the sweeping process.

The doping results agree with some earlier studies in showing that lithium and sodium ions are transported more easily through quartz than are potassium ions; on the other hand, the results disagree with those studies concluding that potassium ions are not transported at all in quartz.

Further, it has been shown that qualitative information about the sweeping process can be obtained rapidly by a technique for measuring the Q of the swept samples. These measurements agree with more quantitative results in showing that sweeping quartz improves the Q over a range of temperatures. The study also sheds some light on the effects of doping with alkali ions, showing generally that doping reduces the Q; and in particular, the measurements yield additional evidence that potassium, however weakly, can be electrodiffused in quartz.

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